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Powder Metal Technologies and Applications

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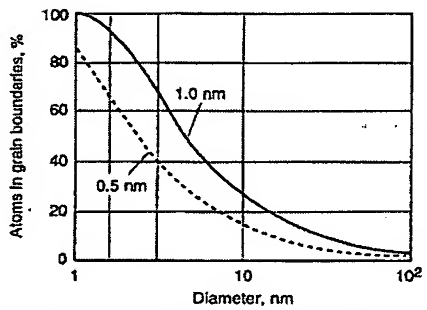

Fig. 10 Percentage of atoms in grain boundaries of a nanophase material as a function of grain diameter, assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm, that is, ~2 to 4 atomic planes wide. Source: Ref 11

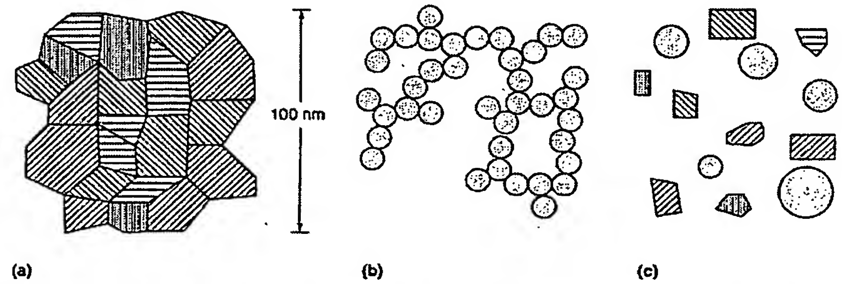

Fig. 11 Three different types of nanoscale materials: (a) nanocrystalline material, (b) agglomerated nanopowder, and (c) nanosuspension

has an effect on quality and permeability. A higher binding agent content improves quality within certain limits, but also reduces the permeability.

Table 7 Comparison of the most frequently used gas phase methods for production of metal nanopowders

Method	Advantage	Disadvantage	Typical capacity
Flame reaction	Large output	Broad distribution of particle size, ionic impurities	>1 tonne/day
Plasma reaction	Large output	Broad distribution of particle size, ionic impurities	> 1 tonne/day
Chemical vapor reaction	Narrow distribution of particle size	Ionic impurities	200 kg/day
Inert gas condensation	No impurities	Small output	<10 kg/day

Metallic Nanopowders

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Today there are a number of established applications of ultrafine powders or nanocrystalline materials. At present, applications are essentially limited to magnetic recording media and nanocrystalline soft magnetic materials used in transformer cores (Ref 11, 12). However, the potential applications in advanced engineering and technology are numerous. Some of the applications already under development are:

- Electrically conductive inks or pastes
- Catalysts
- Sintering accelerators
- Microfilters
- Magnetic recording media
- Magnetic fluids
- High-strength/high-temperature construction materials
- Nanocomposites
- Drug carriers
- Radar absorbing coatings
- Wear-resistant coatings (tool materials)

Compared to ceramic processing, metal nanopowders are much more difficult to process and handle than powders in the micron size range. Nevertheless, different applications require metallic nanopowders and different production processes to serve this need. This Section provides an introduction in the different processes commercially used to produce metal nanopowders with specific emphasis on gas phase techniques for production of powders with a low-impurity level. Example applications describe the state-of-the-art methods in using metal nanopowders in industry.

The term nanopowder is usually used to describe powders with a particle diameter of <1 μm = 1000 nm (Fig. 1). Nanoscale powders have been used in the paint coating industry in tremendous volumes for decades—if made from carbon and metal oxides. Pigment soot, also named carbon black, is a carbon nanoscale powder with particle size 10 to 100 nm and is probably the most prominent example of this type of nanopowder. Nanoscaled silica powders are used as filler additives for a variety of organic suspensions in order to tailor their rheological behavior. The use of ultrafine carbide and nitride powders provides hardmetal tools with a remarkable increase in bending strength resulting in an extended time to failure.

The term nanopowder is also used to designate important changes in properties with the reduction of particle size. In this context the term is sometimes used for powders smaller than a certain threshold, where a dramatic change in properties occurs. Changes in properties can be caused, for example, by the increase in surface atoms of nanopowders. Figure 10 (Ref 13) shows the relative amount of surface atoms of powder particles as the function of the particle diameter.

Nanoscale materials are used for production of advanced material components in three different types, as shown in Fig. 11. A nanocrystal or nanocrystalline material is a dense material with grain sizes in the nanometer range. Nanopowder is often used as aggregated powder particles, either as a suspension or as a loosely packed layer. A nanosuspension, or nanodispersion, is usually the name for a suspension of single nanoparticles, either in a liquid or in a solid matrix (Ref 14).

Production Methods

The production techniques used for fine (micron scale) powders generally fail in the submicron (nanometer) range. Methods like gas or water atomization have a lower particle size limit of ~1 to 5 μm. Milling is used for particle size reduction of very brittle materials like tungsten carbide or ceramics, but fail for ductile materials like precious metals.

A variety of methods are available for the production of ultrafine powders with submicron particle size. Gas phase reactions, spray drying, or precipitation methods are used most frequently. Thousands of tons of ceramic nanopowders have been produced for decades basically via thermal decomposition from the gas phase (aerosol process). One of the basic principles is the inert gas condensation (IGC). With IGC, high-quality powders with low chemical impurities from precursor materials, and low amounts of oxides or nitrides from the production process can be produced. Other principles like flame reduction or plasma reduction use the decomposition and reduction of metal salts in a gas flame or plasma. The chemical vapor reaction (CVR) process uses the reaction of metal chlorides and hydrogen in a hot wall reactor.

Table 7 gives a comparison of the most commonly used four basic methods in gas phase production of metal nanopowders. Information from approximately twelve companies active in production of metal nanopowders for industrial applications is the source of the different production techniques in Table 7. Additional companies are active in producing powders by liquid-phase techniques or by ball milling (Table 8).

The method used most frequently for the production of dry metal nanopowders with very low impurity content is based on the condensation of a supersatured metal vapor in the presence of a

nonreacting cooling gas such as helium. This method is described in more detail in the next section.

Inert Gas Condensation

The IGC method is performed by evaporating and condensing of the respective material in a vacuum cylinder filled with a low pressure of an inert gas (e.g., 10 mbar helium). Evaporation of the respective material can be completed by magnetron sputtering, electron beam, laser, or Joule heating of a crucible. The vapor nucleates homogeneously due to collisions with the cold inert gas atoms. The growth of particles within the convection gas flow occurs basically via coalescence. This type of growth process is intrinsic and leads to a Gaussian distribution of the resulting particle sizes on a logarithmic scale. The size of the primary particles that are agglomerated in a chain or network-like structure can be controlled via the type and pressure of the inert gas within approximately one to two orders of magnitude. Via thermophoretic effects, the particle fog condenses preferably on cooled substrates that are implemented into the container, for example, in the form of rotating stainless steel container filled with liquid nitrogen. The particles build up a flaky powder layer on the cooling wall and can be removed continuously by a scraper.

The fundamentals of the gas phase evaporation process are well understood and used for several process variations. Figure 12 shows the sketch of equipment used in a lab scale environment by Fraunhofer for production of precious metals nanopowders with a rate of ~1 to 2 kg/day.

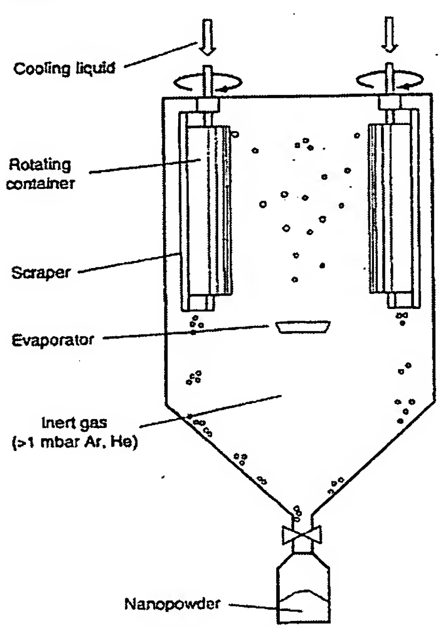

Fig. 12 Sketch of pilot scale equipment to produce metallic nanopowders with the inert gas condensation technique. Source: Ref 14

Table 8 Overview on production processes used in industry

Production process	Number of companies (different processes possible)	Main products
Gas phase processes		
Inert gas condensation	4	Precious metals, Ni, Fe, Pt, semiconductor powders
Chemical vapor condensation	2	Ta and other refractory metals, semiconductor powders
Precipitation	3	Precious metals
Plasma or flame enhanced chemical vapor condensation	3	Mainly ceramics, side products are precious metals and others
Spray condensation	3	Carbides
Chemical precipitation in the liquid phase	5–10	Precious metals
Milling processes	~6	Carbides

Process Variations in Inert Gas Condensation. Several variations of the process exist, for example, evaporation in a reactive gas instead of an inert gas and formation of the respective nitrides or oxides of an evaporated metal. Other variations of the process are using an enforced gas flow transporting the particles to a porous substrate, where the particles are separated from the carrier gas. Additionally to these variations, the powder produced in the gas phase can be deposited on different substrates depending on the planned application. Figure 13 shows the process variations possible for production of dry powder, dense pressed parts, dispersions, or filter applications.

Quality Affecting Factors in Production of Metallic Nanopowders. The main problems in production and processing are caused by the small particle size and the corresponding high specific surface area of nanopowders. As a main quality issue, the pickup of oxides or nitrides during processing or storage need to be pre-

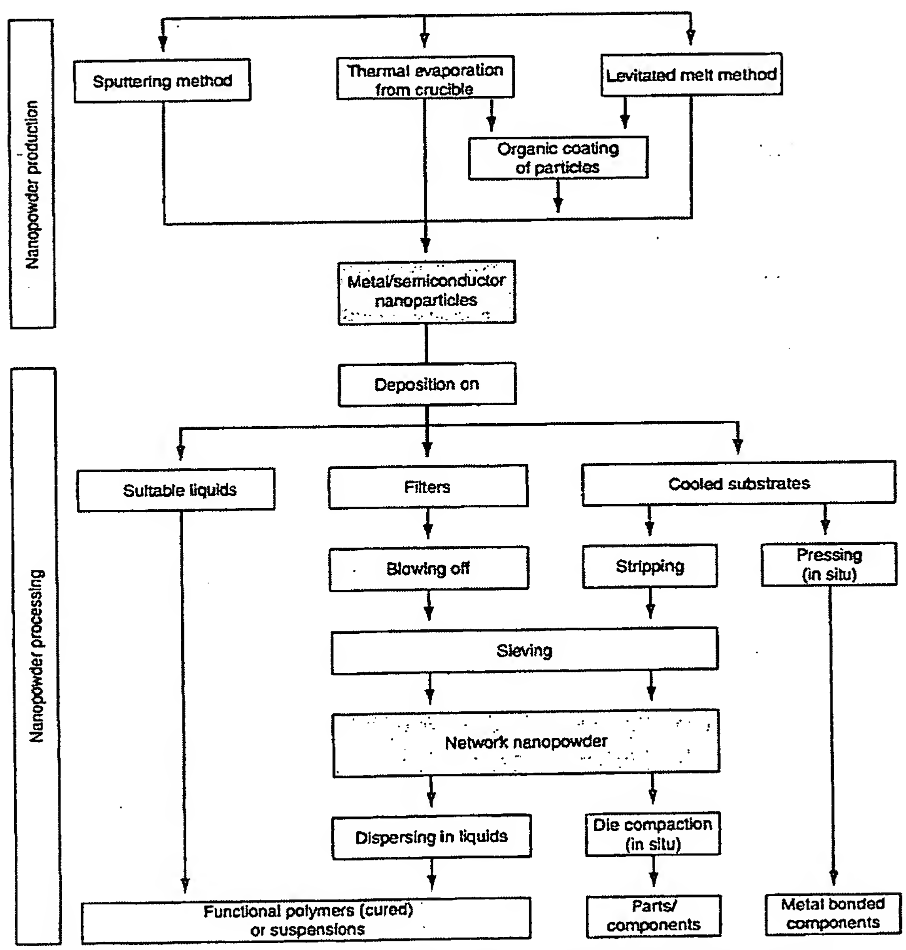

Fig. 13 Process variation of the inert gas condensation for production of different types of nanoscale materials

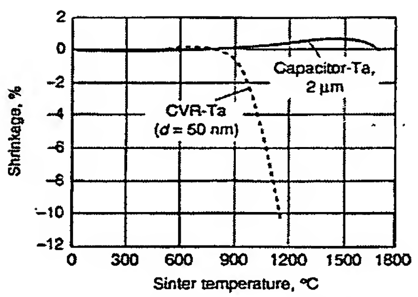

Fig. 14 Decrease in sinter temperature of a tantalum nanopowder with decreasing powder particle size. Source: Ref 16

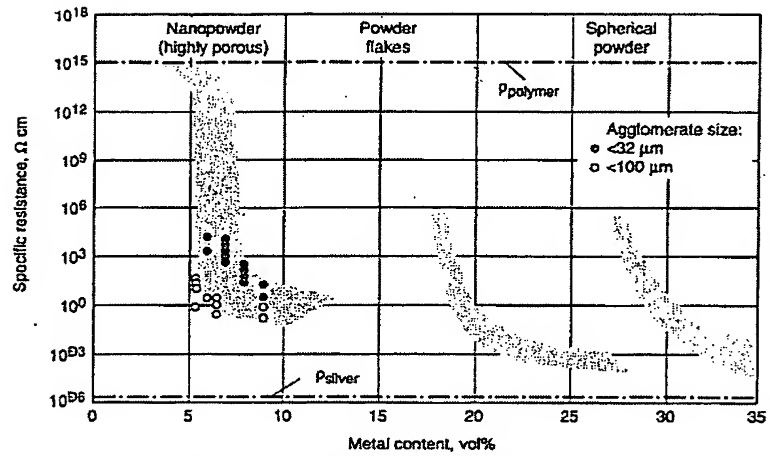

Fig. 15 Shift of the percolation threshold of electrical conductivity in filled polymers by usage of highly porous nanosized powders

vented. As nanopowders are often used or processed in suspension, the degree of agglomeration is also a quality issue due to the need of deagglomeration of the powders. Both factors, the pickup of gaseous impurities and the agglomeration, increase with decreasing particle size. For nanopowders the development of technologies that integrate production and processing steps is essential.

Applications

Because of the very fine grain sizes, nanocrystalline materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained polycrystalline materials. These properties include increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, and superior soft magnetic properties in comparison with conventional coarse-grained materials. All of these properties are being extensively investigated to explore possible applications, and the origin and consequences of some of these properties are discussed in Ref 15.

Dense parts and porous coatings from ceramic nanopowders have attracted interest for decades, and many low-cost processing routes are available. In particular, the use of oxide nanopowders in optics, electronic, and cosmetics, (ultraviolet, UV, protection) is established. Several potential applications of metallic nanopowders are investigated and reported. The following two examples are typical for the use of nanopowders for functional materials.

Applications Based on the High-Sinter Activity of Metallic Nanopowders. With regard to solid state sintering theory and experimental proof, it is well known that a decrease in particle size enhances sinter activity and leads to intense shrinkage of pressed powders at temperatures well below those attained at conventional powder size. This property is particularly useful in electronic packaging technology, where electrically conductive bonding materials play an essential role. The cold welding properties combined with ductility make metal alloy nanopowders suitable sinter aids for metal to metal bonding. The high sinter activity can be usefully applied in diffusion bonding of parts. The nanopowders act as an intermediate layer. It was shown that after the bonding process no welding interface is visible in metallographic cross section.

In particular, sintering of ultrafine refractory metals provides a means to lower the sintering temperature. Due to the fact that the performance of tantalum capacitors is closely related to the specific anode surface area, the use of nanosized tantalum powders at a reduced sintering temperature was investigated (Ref 16). Figure 14 shows the decrease in sintering temperature obtained by use of 50 nm powder for tantalum capacitors compared with standard quality 2 µm powder.

Nanopowder-Polymer Composites for Microelectronic Applications. Metallic filling powders in polymers play an important role for the realization of electrical conductive adhesives, radio frequency shielding polymers, or magnetic polymeric layers. In most applications, the use of high-aspect ratio fibers and flakes is advantageous.

A reduction of the relative amount of metal powder in an electrical conductive adhesive or polymer is possible by using porous nanoscale powders (Fig. 15). With this reduction of filler volume, adhesives with a better thermo-cycling behavior can be produced for applications in automotive microelectronics (Ref 17).

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